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<b>(21) International Application Number:</b> PCT/EP97/01193 <b>(22) International Filing Date:</b> 10 March 1997 (10.03.97)  <b>(30) Priority Data:</b> 08/616,316                      15 March 1996 (15.03.96)                      US  <b>(71) Applicant:</b> RHONE-POULENC AGROCHIMIE [FR/FR]; 14/20, rue Pierre-Baizet, F-69009 Lyon (FR).  <b>(72) Inventors:</b> GRABER, Gérard; 8, rue du Docteur-Bonhomme, F-69003 Lyon (FR). PILLET, Louis; 9, rue Simon-Buisson, F-69410 Champagne-au-Mont-d'Or (FR). LONG, David, Alan; 9407 Laurel Spring Drive, Chapel Hill, NC 27514 (US).  <b>(74) Agent:</b> BRACHOTTE, Charles; Rhône-Poulenc Agrochimie, 14/20, rue Pierre-Baizet, F-69009 Lyon (FR).		<b>(81) Designated States:</b> AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GE, HU, IL, IS, JP, KP, KR, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, TR, TT, UA, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> HERBICIDAL COMPOSITIONS  <b>(57) Abstract</b>  The invention relates to a composition comprising: (a) a herbicidally effective amount of a 4-benzoylisoxazole derivative; (b) a stabilizing amount of a sulfonic acid derivative effective to stabilize said 4-benzoylisoxazole derivative; and (c) at least one partner pesticide.		

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## **HERBICIDAL COMPOSITIONS**

### **Background of the Invention**

5           This invention relates to novel herbicidal compositions comprising a 4-benzoylisoxazole derivative, a partner pesticide and a stabilizing agent.

### **Discussion of Related Art**

10           It is well known in the art of pest control that mixtures of one pesticide with another pesticide can provide an effective level of control of a particular pest problem. For example, in the area of weed control, it is often desirable to use two or more different herbicides having  
15           complementary activity (e.g. where one herbicide controls grass weeds and the other herbicide controls broad leaf weeds) or having a synergistic interaction with each other (which may enable lower dose rates of the herbicides to be used in combination). However, a problem  
20           can arise where the two pesticides are chemically incompatible with each other. This problem may not be very important where the herbicides are only added in a tank mix formulation, where the herbicides are individually present in a large concentration of water in a spray tank; but it is often desirable to provide the user of the herbicide (i.e. a farmer) with a "pre-mix" formulation comprising the two or more  
25           pesticides, as this helps the farmer avoid having to calculate the different quantities of herbicide to be prepared in the tank mix and ensures that the correct application rates of the pesticides are applied to the locus.

          Herbicidal 4-benzoylisoxazoles are disclosed in the literature, for example see European Patent Publication Nos. 0418175, 0487357, 0527036 and 0560482 and Cramp et al United States Patent No.  
30           5,371,064, the contents of which are incorporated herein by reference. Also, these compounds are disclosed in mixture with other pesticides, for example triazine herbicides and chloroacetamide herbicides in International Patent Application Publication Nos. WO95/15691 and WO96/03877 respectively, the contents of which are incorporated herein  
35           by reference. These publications disclose the results of various tank mixture trials of the herbicides which demonstrated a biological synergy between the mixtures.

A problem which can exist with 4-benzoylisoxazoles is their instability under certain conditions. For example, in the presence of bases, the compounds can undergo ring opening to give a 2-cyano-1,3-dione compound. This can lead to difficulties in producing pre-mixed formulations containing an isoxazole and a partner pesticide. It is therefore an object of the present invention to provide a composition comprising an isoxazole derivative having an improved stability.

### **Summary of the Invention**

Therefore the present invention provides a composition comprising:

- (a) a herbicidally effective amount of a 4-benzoylisoxazole derivative;
  - (b) a stabilizing amount of a sulfonic acid derivative effective to stabilize said 4-benzoylisoxazole derivative; and
  - (c) at least one partner pesticide;
- wherein the composition comprises at least one liquid phase.
- Surprisingly, the applicants have found that the presence of a sulfonic acid derivative provides a stabilizing effect on the 4-benzoylisoxazole derivative in these compositions.

### **Description of Preferred Embodiments**

In the description that follows, unless otherwise specified, the percentages are by weight.

The composition of the invention generally contains up to about 85%, especially up to about 75%, of active ingredient (i.e. components (a) and (c) above), although it will be understood that this amount may vary depending on the nature of the composition and the solubility and dispersibility of the various components. Preferably the composition contains up to about 55 % of active ingredient, more preferably from about 20 to about 55%.

By the term "sulfonic acid derivatives" is meant compounds containing at least one (preferably one or two) -SO<sub>3</sub> moieties. The sulfonic acid derivative may be in the form of a free acid or a salt.

Examples of sulfonic acid derivatives include alkyl aryl sulfonic acid, such as dodecylbenzene sulfonic acid, C<sub>16-24</sub> benzene sulfonic acids, xylene or toluene sulfonic acids, and benzene sulfonic acid; other aromatic sulfonic acids such as naphthalene sulfonic acid; alkyl aryl ether disulfonic acids, such as dodecyl diphenyl oxide disulfonic acids; sulfuric acid; or salts thereof (e.g. sodium bisulfate). Dodecylbenzene sulfonic acid and aryl ether disulfonic acid derivatives are particularly preferred. Particularly preferred salts are alkali and alkaline earth metal salts (e.g. sodium and calcium salts). Where the composition is in the form of an emulsion concentrate, the calcium salt is generally preferred. Where the composition is in the form of a suspension concentrate, the sodium salt is generally preferred.

It will be understood that in certain cases the stability of the partner pesticide may also depend on factors such as pH, and that the pH of the mixture may need to be adjusted by the skilled worker accordingly. Preferably the pH of the composition is in the range from about 2 to about 7, more preferably from about 2.0 to about 5.0.

Generally the amount of sulfonic acid derivative present is from about 0.01 to about 15% of the composition weight, although the exact amount may vary depending on the specific sulfonic acid derivative present, the stability of the partner pesticide, and the nature of the other formulants present.

It will be understood that in this description the term 'liquid' includes thickened liquids and gels. The compositions of the invention are preferably provided in the form of pre-mixed formulations. Preferred formulations are emulsifiable concentrates, suspension concentrates, gels, suspo-emulsions, and emulsion concentrates (e.g. either oil-in-water or water-in-oil emulsions). Compositions in the form of emulsifiable concentrates or suspension concentrates are particularly preferred.

When in the form of an emulsifiable concentrate the composition generally includes a primary solvent [to dissolve the isoxazole component (a), although in some cases it is also needed to dissolve the partner pesticide (c)], which is generally a polar solvent. Suitable primary solvents include ether solvents (e.g. tetrahydrofuran); dimethyl phthalate; acetonitrile; ketone solvents (e.g. butyrolactone, acetophenone, isophorone or cyclohexanone); and phosphates (e.g.

tributyl or triethyl phosphates). Particularly preferred primary solvents are ketones, most preferably cyclohexanone or acetophenone. Generally, the presence of N-methylpyrrolidone as a solvent in emulsifiable concentrate solutions tends to reduce the stability of the compositions of the invention.

The emulsifiable concentrate compositions of the invention typically include a secondary solvent, to help achieve a good emulsion on dilution, as well as keeping the cost of the composition lower (since such solvents are typically cheaper than the primary solvent). The secondary solvent can also, in some cases, contribute to the solvency of the composition. This secondary solvent is usually non-polar, and representative examples of suitable secondary solvents include aromatic solvents such as Exxon Aromatic 100, Aromatic 150 or Aromatic 200 (trade marks); chlorinated solvents such as chlorinated hydrocarbons (e.g. dichloromethane) and chlorinated aromatic solvents (e.g. chlorinated toluenes; mono- or dichlorobenzenes; or mixtures thereof); and esters such as C<sub>8</sub>-18 (preferably C<sub>8</sub>-10) methylated fatty acids, aromatic esters and methyl salicylate; and ethers. In addition, it has been found that in certain cases, mixtures of two or more secondary solvents (e.g. a methylated fatty acid and chlorinated aromatic solvents) can give particularly stable compositions.

It is also generally desirable to include one or more surfactants in the composition of the invention, which aid the availability of the active ingredient to the weeds to be controlled. Suitable surfactants include:

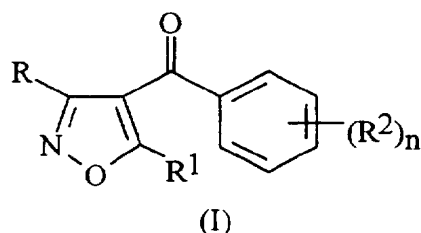
non-ionic surfactants, such as carboxylated alkyl phenols, alkoxylated alcohols, fatty acid alkoxylates, sorbitol and sorbitan alkoxylates and esters, block co-polymers, alkyl phenol alkoxylates, amine alkoxylates, alcohol ethers, alcohol alkoxylates, alkoxylated vegetable oils (e.g. castor oil), and alkoxylated tristyrylphenols (e.g. ethoxylated tristyryl phenols); the latter being most preferred;

and ionic surfactants, especially anionic surfactants. In emulsifiable concentrates preferred ionic surfactants include phosphates esters which may be aryl alkoxylated, alcohol alkoxylated, and triaryl alkoxylated; or sulfosuccinates. It will also be understood that in certain cases sulfonic acid derivatives may also act as ionic surfactants, especially when in the form of salts, such as the calcium salt. In suspension concentrate compositions preferred ionic surfactants include

alcohol ether sulfates, alcohol sulfates, aryl sulfonic acid salts, alkyl aryl ether sulfates, naphthalene sulfates and salts of naphthalene sulfonic acids, and lignosulfonates.

The surfactants are preferably present in an amount from about 0.01 to about 20% of the composition weight, especially in emulsifiable concentrate formulations, preferably from about 2 to about 6% (e.g. about 2 to about 5%).

Preferably the 4-benzoylisoxazole derivatives has the formula (I):



wherein

R is hydrogen or  $-\text{CO}_2\text{R}^3$ ;

$\text{R}^1$  is cyclopropyl;

$\text{R}^2$  is halogen,  $-\text{S}(\text{O})_p\text{Me}$ ,  $\text{C}_{1-6}$  alkyl or  $\text{C}_{1-6}$  haloalkyl,

n is two or three;

p is zero, one or two; and

$\text{R}^3$  is  $\text{C}_{1-4}$  alkyl.

In formula (I) above, compounds in which n is three and the groups  $(\text{R}^2)_n$  occupy the 2,3 and 4-positions of the benzoyl ring; or in which n is two and the groups  $(\text{R}^2)_n$  occupy the 2 and 4- positions of the benzoyl ring are preferred.

Compounds of formula (I) above in which each  $\text{R}^2$  is halogen,  $-\text{S}(\text{O})_p\text{Me}$  or trifluoromethyl are also preferred.

Preferably one of the groups  $\text{R}^2$  is  $-\text{S}(\text{O})_p\text{Me}$ .

Even more preferably, the compound of formula (I) is selected from

A. 5-cyclopropyl-4-(2-methylsulfonyl-4-trifluoromethyl)benzoylisoxazole;

B. 5-cyclopropyl-4-(4-methylsulphonyl-2-trifluoromethyl)benzoylisoxazole;

C. 4-(2-chloro-4-methylsulfonyl)benzoyl-5-cyclopropylisoxazole;

D. 4-(4-chloro-2-methylsulfonyl)benzoyl-5-cyclopropylisoxazole;

E. 4-(4-bromo-2-methylsulfonyl)benzoyl-5-cyclopropylisoxazole,

F. ethyl 5-cyclopropyl-4-(2-methylsulfonyl-4-trifluoromethyl)benzoylisoxazole-3-carboxylate, and

G. ethyl 5-cyclopropyl-4-(3,4-dichloro-2-methylsulfonyl)benzoylisoxazole-3-carboxylate.

The letters A to G are assigned to these compounds for reference and identification hereafter. Compound A is most preferred.

The partner pesticide may be a fungicide, an insecticide, a plant growth regulator or, most preferably, a herbicide. More preferably the partner pesticide is selected from a chloroacetamide herbicide, a triazine herbicide and a 2,6-dinitroaniline herbicide.

Where the partner herbicide is a chloroacetamide herbicide, it is preferably of formula (II):



wherein

R<sup>31</sup> represents hydrogen, C<sub>1-6</sub> alkyl, C<sub>1-6</sub> haloalkyl, C<sub>1-6</sub> alkoxy or C<sub>1-6</sub> alkoxyalkyl; or alkenyl, haloalkenyl, alkynyl, haloalkynyl or acylamidoalkyl, each having up to six carbon atoms;

Ar represents thienyl or phenyl optionally bearing one or more substituents selected from the group consisting of halogen, amino, C<sub>1-6</sub> alkyl, C<sub>1-6</sub> haloalkyl, C<sub>1-6</sub> alkoxy and C<sub>1-6</sub> alkoxyalkyl.

In certain cases the groups Ar and R<sup>31</sup> can give rise to optical and/or stereoisomers. All such forms are embraced by the present invention.

The chloroacetamide herbicide preferably is selected from acetochlor and metolachlor [including all mixtures of two or more of the four stereoisomers and also individual isomers, such as S-2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide, as described in European Patent Publication No. 077755] propalachlor, alachlor and dimethenamid. Most preferably it is selected from acetochlor, dimethenamid and metolachlor.

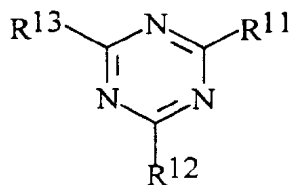
Preferably the weight ratio of isoxazole: chloroacetamide herbicide is from about 1:1 to about 1:80, preferably from about 1:8 to about 1:40; more preferably from about 1:8 to about 1:20, even more preferably about 1:10 to about 1:18.



Where the composition is in the form of an emulsifiable concentrate and the chloroacetamide is acetochlor, the stabilizing agent is preferably an aryl ether disulfonic acid, such as dodecyl diphenyl oxide disulfonic acid; and the primary solvent is preferably acetophenone.

Also, the amount of sulfonic acid stabilizer present is preferably from about 0.1 to about 0.4% (in the case of acetochlor); and from about 0.1 to about 2% (in the case of metolachlor).

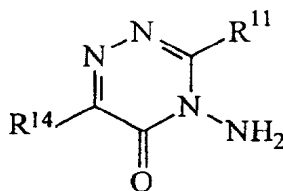
Where the partner pesticide is a triazine herbicide, it is preferably of formula (IIIa):



(IIIa)

wherein  $R^{11}$  represents chlorine or straight- or branched- chain alkylthio or alkoxy having from one to six carbon atoms;  $R^{12}$  represents azido, and mono( $C_{1-6}$ )alkylamino, ( $C_{1-6}$ )dialkylamino or ( $C_{3-7}$ )cycloalkylamino, in which the alkyl and cycloalkyl moieties optionally bear one or more substituents selected from cyano and  $C_{1-6}$  alkoxy; and  $R^{13}$  represents straight- or branched- chain N-alkylamino having from one to six carbon atoms;

or of formula (IIIb):



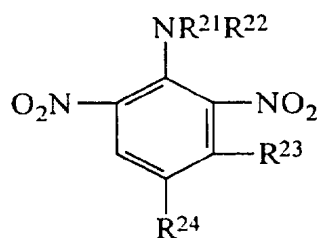
(IIIb)

wherein  $R^{14}$  represents straight- or branched chain alkyl having from one to six carbon atoms and  $R^{11}$  is as defined with formula (IIIa)

Preferred triazine herbicides include terbuthylazine, terbutryn, simazine, cyanazine, atrazine and metribuzin, preferably atrazine.

Preferably the nitroaniline herbicide is a compound of the formula (IV):

- 8 -



(IV)

wherein:

 $\text{R}^{21}$  represents:-

straight or branched chain alkyl or alkenyl having up to 12 carbon atoms which is optionally substituted by one or more halogen atoms or  $\text{C}_{3-7}$  cycloalkyl groups;

$\text{R}^{22}$  represents hydrogen or a group  $\text{R}^{21}$  as defined above,  $\text{R}^{21}$  and  $\text{R}^{22}$  being the same or different;

 $\text{R}^{23}$  represents:-

hydrogen or halogen;

straight or branched- chain alkyl having from 1 to 12 carbon atoms which may be substituted by one or more halogen atoms; or  
an unsubstituted amino group;

 $\text{R}^{24}$  represents:-

halogen;

straight or branched chain alkyl having from 1 to 12 carbon atoms which is optionally substituted by one or more halogen atoms;

straight or branched- chain alkylsulfonyl having from 1 to 12 carbon atoms which is optionally substituted by one or more halogen atoms;

or sulfamoyl.

The groups  $\text{R}^{21}$ ,  $\text{R}^{22}$ ,  $\text{R}^{23}$  and  $\text{R}^{24}$  may give rise to optical and/or geometric isomers. All such forms are embraced in the present invention.

Especially preferred compounds of formula (IV) are:-

2,6-dinitro-N,N-dipropyl-4-(trifluoromethyl)benzeneamine and  
N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzeneamine,

which are known respectively as trifluralin and pendimethalin, pendimethalin being most preferred.

In a further preferred feature of the invention the composition of the invention comprises two partner herbicides, preferably a chloroacetamide herbicide and a triazine herbicide, particularly atrazine. Particularly preferred partner herbicides are

- 5           (a)     acetochlor and atrazine;  
          (b)     metolachlor and atrazine; or  
          (c)     dimethenamid and atrazine.

The weight ratio of isoxazole: chloroacetamide herbicide : triazine herbicide in such formulations is preferably about 1:10:13.

10           The compositions of the invention may also contain other additives, for example fertilizers or safeners. Where the partner pesticide is a chloroacetamide herbicide, preferred safeners include benoxacor, dichlormid, furilazole, flurazole and R-29148.

15           The following non-limiting Examples illustrate the invention. In the text that follow the following trade marks appear:

<u>Trade name</u>	<u>Description</u>	<u>Chemical composition</u>
Witco 5300-50B	Mixture of anionic and non-ionic surfactants	Calcium DBSA with carboxylated alkyl aryl phenol
Biosoft 100	Stabilizer	Linear DBSA (free acid)
Henkel Caprate-Caprylate	Solvent	C <sub>8-10</sub> methyl ester
Soprophor S-25 or Soprophor 796P	non-ionic surfactant	alkoxylated tristyryl phenol
Aromatic 150	Solvent	Aromatic hydrocarbon mixture
Calfax 10LA75	Stabilizer	75% Dodecyl diphenyl oxide disulfonic acid:- linear alkyl
Calfax DBA70	Stabilizer	70% Dodecyl diphenyl oxide disulfonic acid:- branched alkyl
Rhodacal 60 BE or Rhodacal 60BHF	Sulfonic acid stabilizer	Calcium salt of dodecyl-benzene sulfonic acid, 60%
Rhodasurf DA630	Wetting agent	Ethoxylated alcohol
Foamex	Anti-Foaming agent	Dimethyl polysiloxane
Rhodopol 23	Rheological Structuring Agent	Xanthan gum
Morwet D-425	Dispersant	Condensed formaldehyde-naphthalene sulfonate sodium salt
Proxel GXL	Preservative	2-Methyl-4-isothiazalin-3-one
Halso 99	Secondary solvent	Mixed 2- and 4-chloro toluenes
Emery 2209	Secondary solvent	C <sub>8-10</sub> methylated fatty acid

5 Compositions comprising a representative isoxazole derivative, Compound A, and various chloroacetamide and triazine herbicides were prepared and their stability analyzed. To determine the stability, the formulations were placed in 10-20 ml glass vials, sealed to prevent any solvent loss; stored at the specified temperature for the specified length of time then removed, allowed to cool to room temperature, sampled and analyzed. The method of analysis was as follows. Each formulation mixture was analyzed for the proportion of Compound A present using standard High Performance Liquid Chromatography (HPLC) technology. This involves weighing a known amount of sample into a solvent system of acetonitrile:water followed by injecting a

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known aliquot into the HPLC system. If the method calls for an internal standard in which to calibrate accuracy, then the internal standard is added to the extracted aliquot. The extracted sample is passed through a column (either a Zorbax{trade mark} C-18 or Phenyl column) packed with sorbent. Following elution the various components of the composition are separated depending upon varying sorption capacities/hydrophilicity. The amount of the component is determined by the amount of ultraviolet light. The amount of degradation is calculated based upon the difference between the initial and stored analyzed component content.

### **EXAMPLE 1**

This example illustrates the stabilizing effect of the sulfonic acid derivatives of the present invention on a suspension concentrate containing an isoxazole derivative (Compound A, 97.8% technical material) and a triazine herbicide (atrazine, 97.3% technical material). In this case the sulfonic acid stabilizer is sodium bisulfate, and the compositions were stored at 54°C and analyzed after 14 days and 50°C for 1 month.

**Results****Table 1**

<b>Ingredient</b>	<b>Without Sodium bisulfate</b>	<b>With Sodium Bisulfate</b>
Compound A	3.33	3.33
Atrazine	44.6	44.6
Propylene glycol	5	5
Rhodorsurf DA-630	1	1
Foamex AD300	0.3	0.3
Morwet D-425	2.2	2.2
Citric acid	0.63	0
Disodium phosphate	0.54	0.67
Proxel GXL	0.1	0.1
<b>Sodium bisulfate</b>	<b>0</b>	<b>0.54</b>
Water	to 100%	to 100%
% Degradation Cpd A after 2 weeks/54°C	9.7	3.3
% Degradation Cpd A after 1 month/50°C	16.1	3.3

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**EXAMPLE 2**

**Emulsifiable concentrate formulations of Compound A with  
metolachlor and various sulfonic acid derivatives**

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In this Example, various formulations containing metolachlor (technical material) and Compound A (97.5% technical material) were prepared and analyzed to determine the stability of the active ingredients. In each case the following ingredients were present:

- 13 -

Ingredient	Percentage (by weight)
Compound A	3.6
Metolachlor	36.4
Soprophor S-25	5
Cyclohexanone	18
Sulfonic acid derivative	as indicated below
Aromatic 150	to 100%

The results in these tables indicate the percentage of Compound A degraded after 24 hours at 80°C. In the case where no sulfonic acid derivative was present, the percentage degradation was 33.6%, and the percentage metolachlor degradation was 7.0%.

The results with the various sulfonic acid derivatives were as follows:

**Table 2**

Calfax 10LA75 (75% Dodecyl diphenyl oxide disulfonic acid: - linear)

	Percentage Calfax 10LA75 present by weight				
	0.5	1	1.5	2	2.5
Degradation Compound A	4.49	5.88	3.99	N/D	N/D
Degradation of metolachlor	0	3.04	1.12	N/D	N/D
pH dilution	3.41	3.5	3.42	N/D	N/D

**Table 3**

Calfax DBA70 (70% Dodecyl diphenyl oxide disulfonic acid -  
branched alkyl)

	Percentage Calfax DBA70 present by weight				
	0.5	1	1.5	2	2.5
Degradation Compound A	20.9	5.35	3.45	5.38	5.98
Degradation of metolachlor	14.6	1.11	0	1.95	1.13
pH dilution	3.92	3.6	3.38	3.23	3.11

5

**Table 4**

Aristonic acid L (80 - 86 % C<sub>16-24</sub> benzene sulfonic acid: also  
contains 0 to 1% free sulfuric acid)

	Percentage Aristonic acid L present by weight				
	0.5	1	1.5	2	2.5
Degradation Compound A	18.8	12.22	6.25	5.68	7.08
Degradation of metolachlor	10.6	6.72	0.84	0	2.23
pH dilution	4.02	3.64	3.43	3.29	3.18

10



**Table 5**

Para-toluene sulfonic acid (PTSA)

	Percentage PTSA present by weight				
	0.5	1	1.5	2	2.5
Degradation Compound A	12.2	6.53	5.4	7.82	N/D
Degradation of metolachlor	6.96	1.96	1.69	4.97	N/D
pH dilution	3.55	3.25	3.05	2.89	N/D

5

**Table 6**

2-Naphthalene sulfonic acid (2-NSA)

	Percentage 2-NSA present by weight				
	0.5	1	1.5	2	2.5
Degradation Compound A	9.04	4.27	3.38	3.9	N/D
Degradation of metolachlor	4.21	0	1.66	4.12	N/D
pH dilution	3.53	3.31	3.2	2.88	N/D

**Table 7**

Sulfuric acid

	Percentage sulfuric acid present by weight				
	0.1	0.2	0.3	0.4	0.5
Degradation of Compound A	6.32	8.02	7.43	9.62	10.8
Degradation of metolachlor	1.11	5.57	5.0	6.98	9.72
pH dilution	3.99	3.78	3.66	3.34	3.27

5 In each case there was clearly a significant stabilizing effect of the isoxazole provided by the various sulfonic acid derivatives when compared with the unstabilized formulation.

**EXAMPLE 3**

10 The following experiments further illustrate the effect of the sulfonic acid derivatives on the stability of emulsion concentrate compositions comprising an isoxazole derivatives in combination with metolachlor. Tests 1 to 3 below are examples in the absence of a sulfonic acid derivative; tests 4 to 8 are examples in the presence of a  
15 sulfonic acid derivative. In each case the figures represent the weight (in grams) of ingredient present. The formulations were stored at 80°C for 24 hours then analyzed for degradation of Compound A. The results obtained were as follows:

**Table 8**

<b>Ingredient</b>	<b>Test1</b>	<b>Test2</b>	<b>Test3</b>	<b>Test4</b>	<b>Test5</b>	<b>Test6</b>	<b>Test7</b>	<b>Test8</b>
Compound A	19.5	19.5	19.5	19.5	19.5	19.5	19.5	19.5
Metolachlor	356	182.5	547.5	365	365	182.5	365	365
Rhodacal 60BE	0	0	0	100	50	100	0	0
DBSA	0	0	0	0	0	0	50	25
Soprophor S25	0	0	0	0	50	0	50	25
Solvent	645.5	828	643	545.5	545.5	728	545.5	545.5
% Degradation of Cpd A	30	23	40	13	16	7	3	2

These results clearly demonstrate the stabilizing effect of the sulfonic acid derivatives, as there is a substantial reduction in the degradation of Compound A when one compares Tests 1 to 3 and 4 to 6 with Tests results 7 to 8.

#### **EXAMPLE 4**

##### **Formulations of Compound A with acetochlor and dodecylbenzene sulfonic acid**

Emulsifiable concentrate formulations containing acetochlor (95.7% technical material) and Compound A (97.5% technical material) both with and without a sulfonic acid derivative were prepared and analyzed to determine the stabilizing effect of the sulfonic acid derivative. The formulations contained the following ingredients:

<b><u>Ingredient</u></b>	<b><u>Percentage (by weight)</u></b>
Compound A	3.61
Acetochlor	49.1
Witco 5300-50B	5
Cyclohexanone	18
DBSA Biosofts 100	as indicated below
Henkel Caprate- Caprylate	to 100%

Note: DBSA is dodecylbenzene sulfonic acid. The formulations were stored at 80°C for 24 hours and analyzed as described above. The results obtained were as follows:

**Table 9**

	<b>Percentage DBSA Biosoft 100 present</b>							
	0	0.5	0.75	1	1.25	1.5	1.75	2
% Degradation Compound A	16.76	11.07	7.95	10.79	11.93	11.64	11.36	10.51

These results clearly demonstrate that the presence of a sulfonic acid derivative in the mixture reduces the degradation of the isoxazole derivative.

**EXAMPLE 5**

An emulsifiable concentrate was prepared containing the following materials (note that Compound A was a 98.9% technical material and acetochlor was 92.6% technical material with safeners). The stabilizer used was Calfax 10LA 75.

<u>Ingredient</u>	<u>% by Weight</u>
Compound A	4.2
Acetochlor	47.5
Rhodacal 60 BHF	2.7
Soprophor 796P	3.3
Acetophenone	28.0
Stabilizer	as indicated below
Secondary Solvent	to 100%

The composition was stored either at 80°C for 24 hours, or 54°C for 14 days, and the percentage degradation of the two active ingredients was determined according to the procedures described above.

The results were as shown in Tables 10 and 11 below. In the tables (i) means storage at 80°C for 24 hours and (ii) means storage at 54°C for 14 days.

**Table 10**

Secondary Solvent = Chlorotoluene

Ingredient	Storage	% Stabilizer							
		0.25	0.27	0.30	0.325	0.35	0.37	0.40	0.42
Cpd A	(i)	10.17	8.75	8.27	7.58	7.31	6.87	7.31	6.86
Cpd A	(ii)	13.48	12.06	12.06	10.66	10.38	10.19	10.38	10.17
Acetochlor	(i)	3.62	4.32	4.55	5.91	6.83	7.95	9.07	10.41
Acetochlor	(ii)	0.45	0.91	1.59	2.05	2.96	3.86	4.99	5.88
pH of dilution		4.25	4.17	4.25	4.15	4.09	4.03	3.95	3.83

**Table 11**Secondary Solvent = C<sub>8-10</sub> Methylated Fatty Acid

Ingredient	Storage	% Stabilizer							
		0.25	0.275	0.30	0.325	0.35	0.375	0.40	0.425
Cpd A	(i)	8.51	8.55	8.51	8.25	7.82	7.80	7.82	7.55
Cpd A	(ii)	12.77	11.88	11.58	11.08	10.66	11.11	10.55	11.79
Acetochlor	(i)	3.17	3.85	5.64	7.21	8.13	10.34	11.29	12.36
Acetochlor	(ii)	2.26	2.04	3.39	4.50	5.19	7.19	7.90	8.76
pH of dilution		4.28	4.27	4.30	4.15	4.00	3.93	3.89	3.81

5

**EXAMPLE 6**

An emulsifiable concentrate was prepared containing the following ingredients (Compound A, acetochlor and the stabilizer were as described in Example 5 above).

10

<u>Ingredient</u>	<u>% by Weight</u>
Compound A	2.1
Acetochlor	24.9
Rhodacal	2.7
Soprophor 796P	3.3
Stabilizer	0.15
Secondary Solvent	to 100%

15

The secondary solvents used were Halso 99 (mixed 2- and 4-chlorotoluene) and Emery 2209 (C<sub>8-10</sub> methylated fatty acid). These secondary solvents were present either alone or as a 50:50 mixture of the two solvents. The compositions were stored at 80°C or 24 hours and the percentage degradation of the two active ingredients was determined according to the procedures described above.

20

The results were as follows. The figures in the table indicate the percentage degradation.

**Table 12**

Active Ingredient	Secondary Solvent		
	H	E	E & H
Compound A	1.90	4.72	0.46
Acetochlor	0.43	3.59	0.79

E is Emery 2209; H is Halso 99.

These results indicate that in certain cases mixtures of two secondary solvents provides especially good emulsifiable concentrates.

**Example 7**

The following emulsifiable concentrate was prepared using the active ingredients found in Example 6 above. The stabilizer was Calfax 10LA 75.

<u>Ingredient</u>	<u>% by Weight</u>
Compound A	2.2
Acetochlor	25.0
Rhodacal 60 BHF	3.3
Soprophor 796P	3.3
Stabilizer	as below
Chlorotoluene	to 100%

The compositions of the invention may be used to control the growth of weeds and according to a further feature of the invention there is provided a method for controlling the growth of weeds at a locus which comprises applying to said locus a herbicidally effective amount of a composition as described above.

The compositions were stored and degradation of active ingredients measured as described in Example 5 above. The results obtained are shown in Table 13 below, in which (i) means 80°C at 24 hours and (ii) means 54°C for 14 days.

**Table 13**

<b>Ingredient</b>	<b>Storage</b>	<b>% Stabilizers</b>				
		<b>0</b>	<b>0.1</b>	<b>0.2</b>	<b>0.3</b>	<b>0.4</b>
Cpd A	(i)	5.0	3.17	2.28	2.73	1.82
Cpd A	(ii)	5.91	2.71	4.48	1.36	1.36
Acetochlor	(i)	-1.68	-1.27	3.36	11.34	18.57
Acetochlor	(ii)	-2.52	-3.38	2.52	2.52	2.95

Negative degradation numbers reflect an increase in the active content found in the aged sample compared with the initial sample. This can be attributed to loss of solvent or to analytical variability. Such data should be appreciated by those skilled in the art. Negative degradations are interpreted as stable samples in which there is no degradation.

The compositions of the invention are useful as herbicides and according to a further feature of the present invention, there is provided a method of controlling the growth of weeds at a locus which comprises applying to said locus a herbicidally effective amount of a composition as defined above.



**CLAIMS**

1. A composition comprising:
  - (a) a herbicidally effective amount of a 4-benzoylisoxazole derivative;
  - (b) a stabilizing amount of a sulfonic acid derivative effective to stabilize said 4-benzoylisoxazole derivative; and
  - (c) at least one partner pesticide;wherein the composition comprises at least one liquid phase.
2. A composition according to claim 1 which is provided as a pre-mixed formulation.
3. A composition according to claim 1 or 2 in which the sulfonic acid derivative is selected from an alkyl aryl sulfonic acid, a C<sub>16</sub>-C<sub>24</sub> benzene sulfonic acid, an aryl ether disulfonic acid, sulfuric acid; or a salt thereof.
4. A composition according to claim 1, 2 or 3 in which the stabilizing agent is a dodecylbenzene sulfonic acid derivative.
5. A composition according to any one of claims 1 to 4 in which the percentage by weight of sulfonic acid derivative present in the composition is from about 0.01 to about 15%.
6. A composition according to any one of claims 1 to 5 in which the composition is in the form of an emulsifiable concentrate, a suspension concentrate, a gel, a suspo-emulsion, or an emulsion concentrate.
7. A composition according to claim 6 which is in the form of an emulsifiable concentrate.
8. A composition according to claim 7 in which the composition comprises a primary polar solvent.

9. A composition according to claim 8 in which the primary polar solvent is a ketone.

10. A composition according to claim 8 or 9 in which the composition further comprises a secondary solvent.

11. A composition according to any one of claims 1 to 10 which further comprises a surfactant.

12. A composition according to any one of claims 1 to 6 or 11 which is in the form of a suspension concentrate.

13. A composition according to any one of the preceding claims in which the or each partner pesticide is a herbicide.

14. A composition according to claim 13 in which the or each partner pesticide is selected from a chloroacetamide herbicide, a triazine herbicide and a 2,6-dinitroaniline herbicide.

15. A composition according to claim 13 or 14 in which the partner herbicide is a chloroacetamide herbicide having the formula (II)



wherein

R<sup>31</sup> represents hydrogen, C<sub>1-6</sub> alkyl, C<sub>1-6</sub> haloalkyl, C<sub>1-6</sub> alkoxy or (C<sub>1-6</sub>)alkoxy(C<sub>1-6</sub>)alkyl; alkenyl, haloalkenyl, alkynyl, haloalkynyl or acylamidoalkyl having up to six carbon atoms;

Ar represents thienyl or phenyl optionally bearing one or more groups selected from the group consisting of halogen, amino, C<sub>1-6</sub> alkyl, C<sub>1-6</sub> haloalkyl, C<sub>1-6</sub> alkoxy and (C<sub>1-6</sub>)alkoxy(C<sub>1-6</sub>)alkyl.

16. A composition according to claim 15 in which the weight ratio of isoxazole: chloroacetamide herbicide is from about 1:1 to about 1:80.

17. A composition according to claim 15 or 16 in which the chloroacetamide herbicide is acetochlor, metolachlor or dimethenamid.

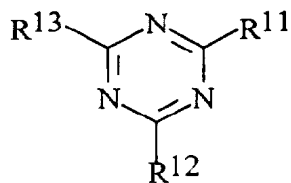
18. A composition according to claim 17 in which the chloroacetamide herbicide is acetochlor.

19. A composition according to claim 15 in which R<sup>21</sup> is 2-methoxy-1-methylethyl and Ar is 2-ethyl-6-methylphenyl.

20. A composition according to claim 19 in which the chloroacetamide herbicide is (RS)-2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide, which is metolachlor.

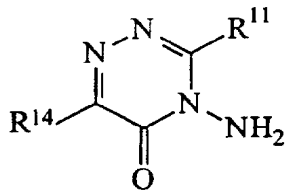
21. A composition according to claim 19 in which the chloroacetamide herbicide is (S)-2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide.

22. A composition according to claim 13 in which the partner herbicide is a triazine herbicide having the formula IIIa:



(IIIa)

wherein R<sup>11</sup> represents chlorine or straight- or branched chain alkylthio or alkoxy having from one to six carbon atoms; R<sup>12</sup> represents azido, mono(C<sub>1-6</sub>)alkylamino, di(C<sub>1-6</sub>)alkylamino or C<sub>3-7</sub> cycloalkylamino, in which the alkyl or cycloalkyl moieties may be optionally substituted by one or more substituents selected from the group consisting of cyano and C<sub>1-6</sub> alkoxy; and R<sup>13</sup> represents straight- or branched- chain N-alkylamino having from one to six carbon atoms; or the formula IIIb:



(IIIb)

wherein  $R^{14}$  represents straight- or branched chain alkyl having from one to six carbon atoms, and  $R^{11}$  is as defined with formula (IIIa).

23. A composition according to claim 22 in which the triazine herbicide is terbuthylazine, terbutryn, simazine, cyanazine, atrazine or metribuzin.

24. A composition according to claim 24 in which the triazine herbicide is atrazine.

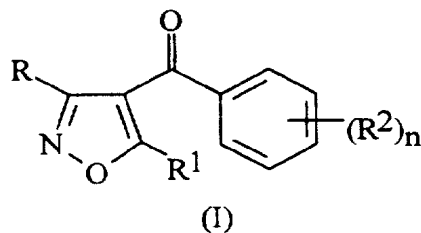
25. A composition according to claim 13 in which there are two partner herbicides.

26. A composition according to claim 25 in which the two partner herbicides are a triazine herbicide and a chloroacetamide herbicide.

27. A composition according to claim 26 in which the partner herbicides are:

- (a) acetochlor and atrazine;
- (b) metolachlor and atrazine; or
- (c) dimethenamid and atrazine.

28. A composition according any one of the preceding claims in which the 4-benzoylisoxazole is an isoxazole derivative having the formula (I):



wherein

R is hydrogen or  $-CO_2R^3$ ;

$R^1$  is cyclopropyl;

$R^2$  is selected from halogen,  $-S(O)_pMe$ , and  $C_{1-6}$  alkyl or  $C_{1-6}$  haloalkyl,

n is two or three; p is zero, one or two; and

$R^3$  is  $C_{1-4}$  alkyl.

29. A composition according to claim 28 in which n is three and the groups  $(R^2)_n$  occupy the 2,3 and 4-positions of the benzoyl ring;  
5 or in which n is two and the groups  $(R^2)_n$  occupy the 2 and 4- positions of the benzoyl ring.

30. A composition according to claim 28 or 29 in which each  $R^2$  is halogen,  $-S(O)_pMe$  or trifluoromethyl.  
10

31. A composition according to claim 28, 29 or 30 in which one of the groups  $R^2$  is  $-S(O)_pMe$ .

32. A composition according to any one of claims 28 to 31 in which the compound of formula (I) is 5-cyclopropyl-4-(2-methylsulfonyl-4-trifluoromethyl)benzoylisoxazole.  
15

33. A composition comprising:

(a) a herbicidally effective amount of 5-cyclopropyl-4-(2-methylsulfonyl-4-trifluoromethyl)benzoylisoxazole;  
20

(b) a stabilizing amount of dodecylbenzene sulfonic acid derivative effective to stabilize said isoxazole; and

(c) at least one partner herbicide which is a chloroacetamide herbicide or a triazine herbicide;  
25

wherein the composition comprises at least one liquid phase.

34. A method for controlling the growth of weeds at a locus which comprises applying to said locus a herbicidally effective amount of a composition as defined in any one of the preceding claims.  
30

35. The use of a sulfonic acid derivative to stabilize a herbicidally effective amount of a 4-benzoylisoxazole derivative.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 97/01193

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 A01N43/80 A01N25/22 //(A01N43/80,43:707,43:70,43:10,37:26,  
37:22,33:18)

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 96 03877 A (RHONE POULENC AGRICULTURE) 15 February 1996 cited in the application see page 22, line 22 - page 23, line 10 ---	1-35
A	EP 0 560 482 A (RHONE POULENC AGRICULTURE) 15 September 1993 cited in the application see page 19, line 50 - page 20, line 56; examples C2,C3 ---	1-35
A	EP 0 645 083 A (AMERICAN CYANAMID CO) 29 March 1995 see page 2, line 45 - page 3, line 14 -----	1-35

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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